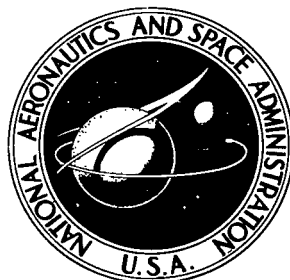


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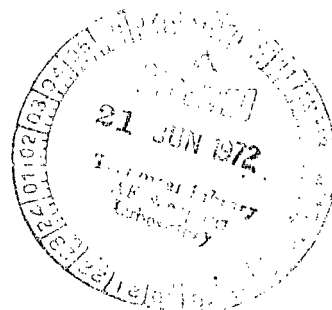


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## THE 1200° C CYCLIC OXIDATION BEHAVIOR OF TWO NICKEL-ALUMINUM ALLOYS (Ni<sub>3</sub>Al AND NiAl) WITH ADDITIONS OF CHROMIUM, SILICON, AND TITANIUM

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16. Abstract <p>The alloys Ni<sub>3</sub>Al and NiAl with and without 1 and 3 atomic percent chromium, silicon, and titanium replacing the aluminum were cyclically oxidized at 1200<sup>0</sup> C for times to 200 hours, and the results were compared with those obtained with the alloy B-1900 subjected to the same oxidation process. The evaluation was based on metal recession, specific weight change, metallography, electron microprobe analysis, and X-ray diffraction. The oxidation resistance of Ni<sub>3</sub>Al was improved by Si, unaffected by Ti, and degraded by Cr. The oxidation resistance of NiAl was slightly improved by Ti, unaffected by Si, and degraded by Cr. The oxidation resistance of Ni<sub>3</sub>Al with 1 atomic percent Si was nearly equal to that of NiAl. Alloy B-1900 exhibited oxidation resistance comparable to that of Ni<sub>3</sub>Al + Cr compositions.</p>					
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# THE 1200<sup>0</sup> C CYCLIC OXIDATION BEHAVIOR OF TWO NICKEL-ALUMINUM ALLOYS (Ni<sub>3</sub>Al AND NiAl) WITH ADDITIONS OF CHROMIUM, SILICON, AND TITANIUM

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## SUMMARY

Nickel-aluminum alloys Ni<sub>3</sub>Al ( $\gamma'$ ) and NiAl ( $\beta$ ) with and without small additions (up to 3 at. %) of chromium, silicon, and titanium replacing the aluminum were cyclically oxidized at 1200<sup>0</sup> C up to 200 hours. The 1200<sup>0</sup> C temperature, although higher than normal superalloy operating temperatures, was chosen to accelerate the oxidation process. Each cycle consisted of 1 hour at temperature followed by 40 minutes of air cooling. Alloy B-1900, a typical  $\gamma'$ -strengthened nickel-base alloy, was given the same exposure for comparison. The degree of attack was judged primarily by metal-recession (metal-loss and depletion-zone) data supplemented by weight-change, metallographic, electron-microprobe, and X-ray diffraction data.

The oxidation resistance of  $\gamma'$  was unaffected by titanium and degraded by chromium. Silicon markedly improved the oxidation resistance of  $\gamma'$ , especially at the 1-atomic-percent level. A sharply defined metal depletion zone was found at the metal-oxide interface in all  $\gamma'$  alloys.

The oxidation resistance of  $\beta$  was unaffected by silicon and degraded by chromium. While titanium additions, especially at the 1-atomic-percent level, substantially reduced spalling, the resultant improvement in oxidation resistance in terms of metal recession was only slight. No depletion zone was found in any of the  $\beta$  alloys.

As a class, the  $\gamma'$  alloys had poorer cyclic oxidation resistance than the  $\beta$  alloys. However, the best of the  $\gamma'$  alloys, Ni-24Al-1Si, was nearly as oxidation resistant as unalloyed  $\beta$ . Alloy B-1900 oxidized as much as Ni-22Al-3Cr.

## INTRODUCTION

The nickel-aluminum (Ni-Al) system is of fundamental importance to nickel-base superalloys. The matrix of such alloys is a nickel-solid solution ( $\gamma$ ), while the main

strengthening phase is  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ). When an oxidation-resistant coating is needed,  $\text{NiAl}$  ( $\beta$ ) is often applied. Chromium (Cr), silicon (Si), and titanium (Ti) are not only commonly present in nickel-base superalloys, but they are also strong oxide formers. These elements are frequently found as major elements in the oxidation products of Ni-base superalloys (ref. 1). An understanding of the oxidation behavior of  $\gamma$ ,  $\gamma'$ , and  $\beta$  and how that behavior is affected by chromium, silicon, and titanium could contribute to an understanding of the oxidation behavior of Ni-base superalloys and their coatings.

While much has been reported on the oxidation of the Ni-Cr system (refs. 2 to 4), little information is available on the Ni-Al system (refs. 3 to 5) and even less on ternary Ni-Al base alloys (refs. 2, 6, and 7).

A systematic high-temperature ( $900^\circ\text{C}$ ) investigation of the Ni-Al system is given by Pettit (ref. 5). Briefly, he found that binary Ni alloys with 31 or more atomic percent Al formed a single external scale of  $\text{Al}_2\text{O}_3$ . The oxidation kinetics were parabolic, with a rate constant about three orders of magnitude less than that of pure Ni. Alloys with less Al formed complex multi-phase scales and were less oxidation resistant. Reference 8 showed that large additions of Cr reduced substantially the amount of Al required to form only  $\text{Al}_2\text{O}_3$ . In the Ni-Al-Si system, only isothermal tests on dilute alloys ( $\gamma$ ) were reported (ref. 9). Between  $1000^\circ$  and  $1200^\circ\text{C}$ , the more oxidation-resistant alloys were those with high Si and Al content. Some  $\gamma$ -phase Ni-Ti alloys were studied (ref. 10) between  $1000^\circ$  and  $1200^\circ\text{C}$ . The data showed that increasing Ti increased the rate of oxidation.

In general, the literature data are predominantly isothermal and for short times ( $\leq 20$  hr). A few cyclic tests were run over 200 hours, but only net weight changes were reported in reference 11.

The current work is an extension of the work of reference 12, which was a systematic study of the oxidation of  $\gamma$ ,  $\gamma'$ , and  $\beta$  alloys with additions of 1, 3, and 10 atomic percent Cr, Si, and Ti. Cyclic and isothermal 100-hour tests were performed in that investigation at  $1100^\circ\text{C}$ . Evaluation of the performance of the alloys was based primarily on weight change and metal recession. The three major findings of the investigation reported in reference 12 were (1) all  $\gamma$  alloys had poorer oxidation resistance than pure Ni had, (2) only 1- and 3-atomic-percent-Si additions improved the oxidation resistance of  $\gamma'$ , and (3) 1- and 3-atomic-percent additions of Cr, Si, and Ti had only a small effect on the oxidation resistance of  $\beta$ .

The object of the present work was to more clearly define the effect of small additions (up to 3 at. %) of Si, Cr, and Ti on the cyclic oxidation of  $\gamma'$  and  $\beta$ . Each cycle consisted of 1 hour at temperature followed by 40 minutes of air-cooling. To accelerate the oxidation process,  $1200^\circ\text{C}$  was selected for the test temperature. This was considered to be necessary, since the oxidation rates of the better compositions in reference 12 were near the limits of detection, especially when evaluated by metal-

recession (metal-loss and depletion-zone) measurements. Even at 1200° C, it was found necessary to continue the  $\beta$ -alloy tests to 200 hours to get sufficient oxidation in order to rank the alloys. Alloy B-1900, one of the more oxidation-resistant superalloys, and one in which  $\gamma'$  is the major phase ( $\sim 65$  vol. %), was also tested for comparison. Alloy thickness changes and weight changes were measured. The oxidation products were examined by X-ray diffraction and metallography.

## EXPERIMENTAL PROCEDURES

### Sample Preparation

Alloys were prepared by vacuum casting. The chemical analysis of the starting materials is given in table I(a). Nickel was heated to its melting point in an  $\text{Al}_2\text{O}_3$  cru-

TABLE I. - CHEMICAL ANALYSES

(a) Starting materials

Material	Purity, wt. %	Impurities, ppm								
		Si	Fe	Ga	Mn	Mo	Cu	Ca	C	
Nickel rod	99.99	---	--	--	--	--	-	--	46	
Aluminum shot	99.99	60	20	30	--	--	-	--	--	
Chromium pellets	99.999	100	10	--	10	10	5	20	--	
Titanium wire	99.97	250	60	--	--	--	-	--	--	
Silicon ingot	(a)	---	--	--	--	--	-	--	--	

(b) Alloy compositions

Nominal composition, at. %	Actual composition, at. %
$\gamma'$ alloys	
Ni-25Al	Ni-24.9Al
Ni-24Al-1Cr	Ni-24.5Al-0.78Cr
Ni-22Al-3Cr	Ni-22.6Al-2.9Cr
Ni-24Al-1Si	Ni-23.6Al-1.0Si
Ni-22Al-3Si	Ni-22.9Al-2.9Si
Ni-22Al-3Ti	Ni-22.0Al-3.4Ti
$\beta$ alloys	
Ni-50Al	Ni-50.5Al
Ni-49Al-1Cr	Ni-48.8Al-1.1Cr
Ni-47Al-3Cr	Ni-47.6Al-2.6Cr
Ni-49Al-1Si	Ni-48.8Al-1.1Si
Ni-47Al-3Si	Ni-46.8Al-2.9Si
Ni-49Al-1Ti	Ni-49.6Al-1.1Ti
Ni-47Al-3Ti	Ni-47.6Al-3.1Ti

<sup>a</sup>Semiconductor grade.

cible under a vacuum of 1 to 10 torr. The other elements were then added to the Ni melt under 50 torr of argon. The melt was poured into a preheated ( $870^{\circ}\text{C}$ ) zircon mold having 1.9-centimeter- ( $3/4$ -in.-) diameter by 10.2-centimeter- (4-in.-) long cylindrical sample section. The pour temperature was between  $1425^{\circ}\text{C}$  and  $1675^{\circ}\text{C}$ , depending on the composition of the melt. The castings were annealed 24 hours at  $1200^{\circ}\text{C}$  in sealed quartz tubes that had been evacuated and backfilled with argon. The purpose of the annealing treatment was to prevent grain growth during oxidation. The castings were then centerless ground to remove surface scale and to provide a surface finish to 32 rms or better. The cylinders were sliced into 2-millimeter-thick disks, and a hole was drilled or electric discharge machined near the edge of each disk so it could be suspended in the furnace. The flat surfaces were polished to a  $1/2$  micrometer finish. Experience here at Lewis indicates that this surface finish results in reproducible oxidation rates. Before oxidation, material was provided from each casting for chemical analysis, metallography, and X-ray diffraction.

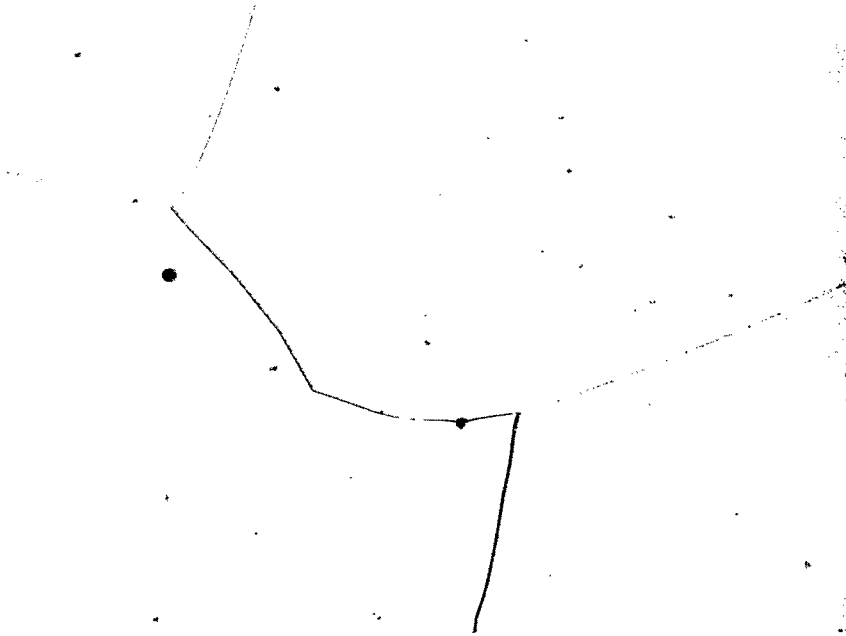
Table I(b) shows that the actual composition in every case is close to the nominal composition. Each composition represents one casting from which came all the oxidation specimens and material for analysis. The nominal compositions are used throughout this report. All compositions are given in atomic percent except where noted.

Typical as-cast microstructures are shown in figure 1. In all cases except the Ni-49Al-1Si, the samples were single phase and large grained. The Ni-49Al-1Si had some second phase, although it was not detected by X-ray diffraction. The X-ray diffraction patterns were all single phase of the kind anticipated from the chemistry of the alloys.

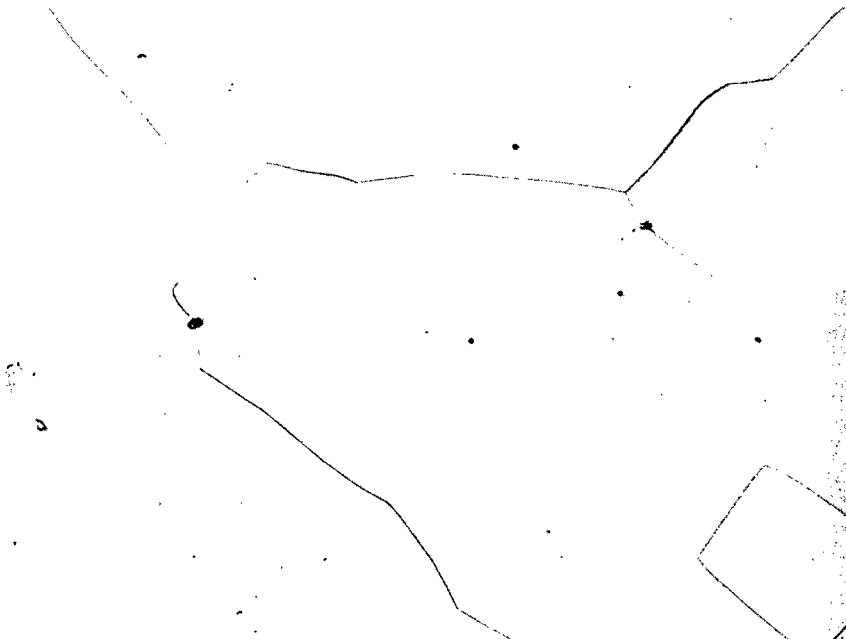
## Testing Procedure

Measurements. - Thickness measurements before oxidation testing were taken at eight positions along the diameter of each specimen with a bench micrometer. After oxidation, the specimens were cross-sectioned along the diameter of the previous measurements, polished, and etched. The thickness of the alloy and the depletion zone when present were measured with a filar eyepiece at approximately the same eight positions. The average of the differences in thickness before oxidation and the thickness of the unaffected alloy after oxidation is taken as the alloy recession. The precision of the thickness measurement, under the best of circumstances, was 0.005 millimeter. Where the interface between the reacted alloy and the unaffected alloy was highly irregular, the accuracy decreased by as much as an order of magnitude.

Cyclic oxidation test. - Cyclic oxidation was carried out at  $1200^{\circ}\text{C}$  in still air for a total time at temperature of up to 200 hours. Each cycle consisted of 1 hour at tempera-



(a) Nickel - 24-aluminum - 1-silicon alloy ( $\gamma'$ ).



(b) Nickel - 49-aluminum - 1-titanium alloy ( $\beta$ ).

Figure 1. - Typical microstructures of as-cast  $\gamma'$  and  $\beta$  alloys. Alloy compositions given in atomic percent. Samples etched; X250.

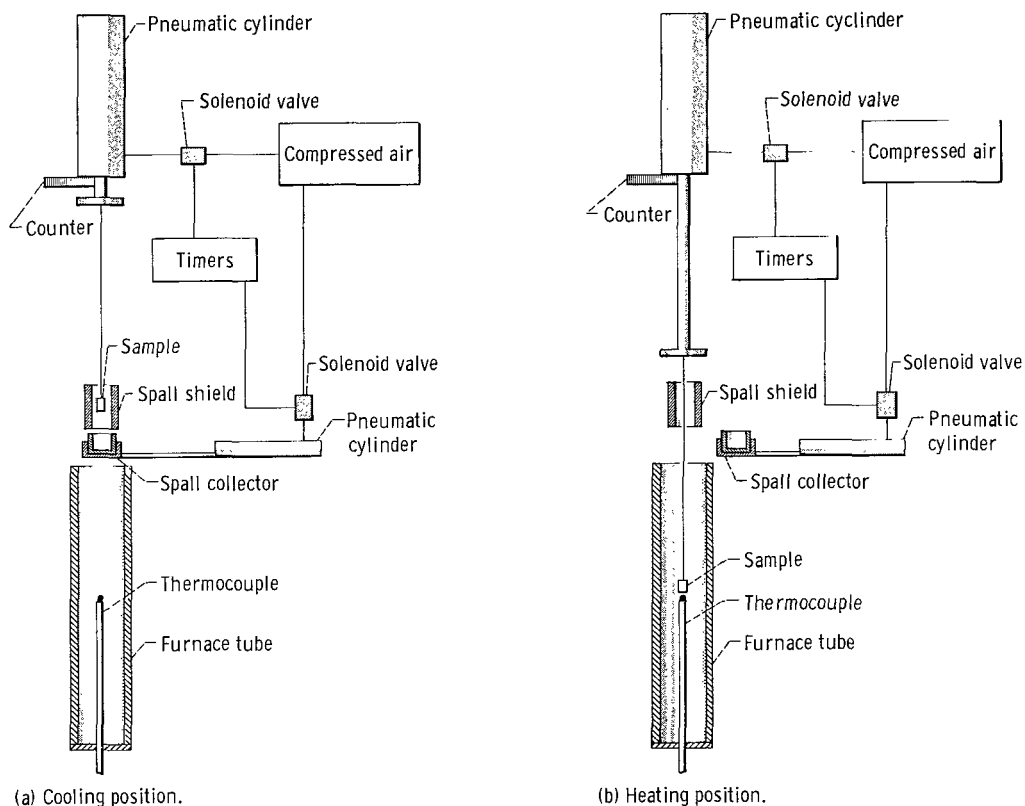


Figure 2. - Automatic cycling and spall-collecting apparatus.

ture followed by 40 minutes of cooling in ambient air outside the furnace. It took  $1\frac{1}{2}$  minutes for the specimens to reach temperature when inserted in the furnace. When withdrawn from the furnace, the specimens cooled to  $550^{\circ}\text{C}$  in 1 minute and reached room temperature in 7 minutes. As shown schematically in figure 2, the samples were automatically cycled in and out of the furnace by a pneumatic cylinder controlled by timers operating solenoid valves. The apparatus was equipped with a spall collector that was automatically positioned under the sample during the cooling portion of each cycle. Thus, spalls could be collected and analyzed. The specimens were periodically weighed between cycles. After oxidation, the specimens were analyzed by X-ray diffraction. The retained scales were X-rayed in situ on the diffractometer, the spalls in the Debye-Scherrer camera. The cross section of each specimen was examined metallographically. The etchant in each case consisted of 92 parts hydrochloric acid, five parts sulfuric acid, and three parts nitric acid.

## RESULTS AND DISCUSSION

The alloys  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ) and  $\text{NiAl}$  ( $\beta$ ) with and without small additions (up to 3 at. %) of Cr, Si, and Ti were cyclically oxidized at  $1200^\circ\text{C}$  for up to 200 hours. Each cycle consisted of 1 hour at temperature in static air followed by 40 minutes of air cooling. Alloy B-1900 was similarly oxidized for comparison. Specific-weight change, X-ray diffraction, metallographic, electron-microprobe, and metal-recession data were obtained. The results of this investigation are presented in the following sections.

### Specific-Weight Change

The specific-weight-change results are shown in figures 3 and 4. All  $\gamma'$  alloys and the B-1900 alloy consistently lost weight. Only the  $\gamma'$  alloys with 1 and 3 atomic percent Si lost less weight than unalloyed  $\gamma'$ . Alloy B-1900 lost more than any other sample.

The weight change of the  $\beta$  alloys was, in general, much less than that of the  $\gamma'$  alloys and of the B-1900 alloy. The exception to this behavior was the  $\beta$  - 3-atomic-

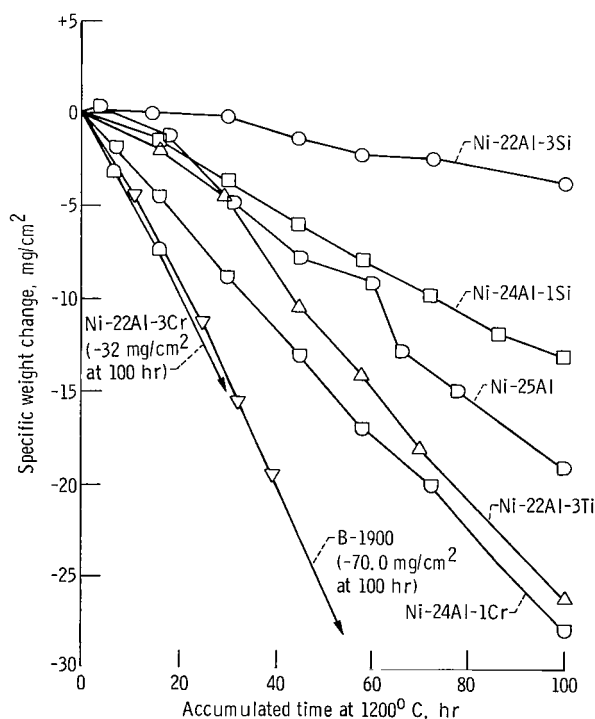


Figure 3. - Cyclic oxidation data for  $\gamma'$  alloys compared with data for the B-1900 alloy. Compositions of alloys given in atomic percent.

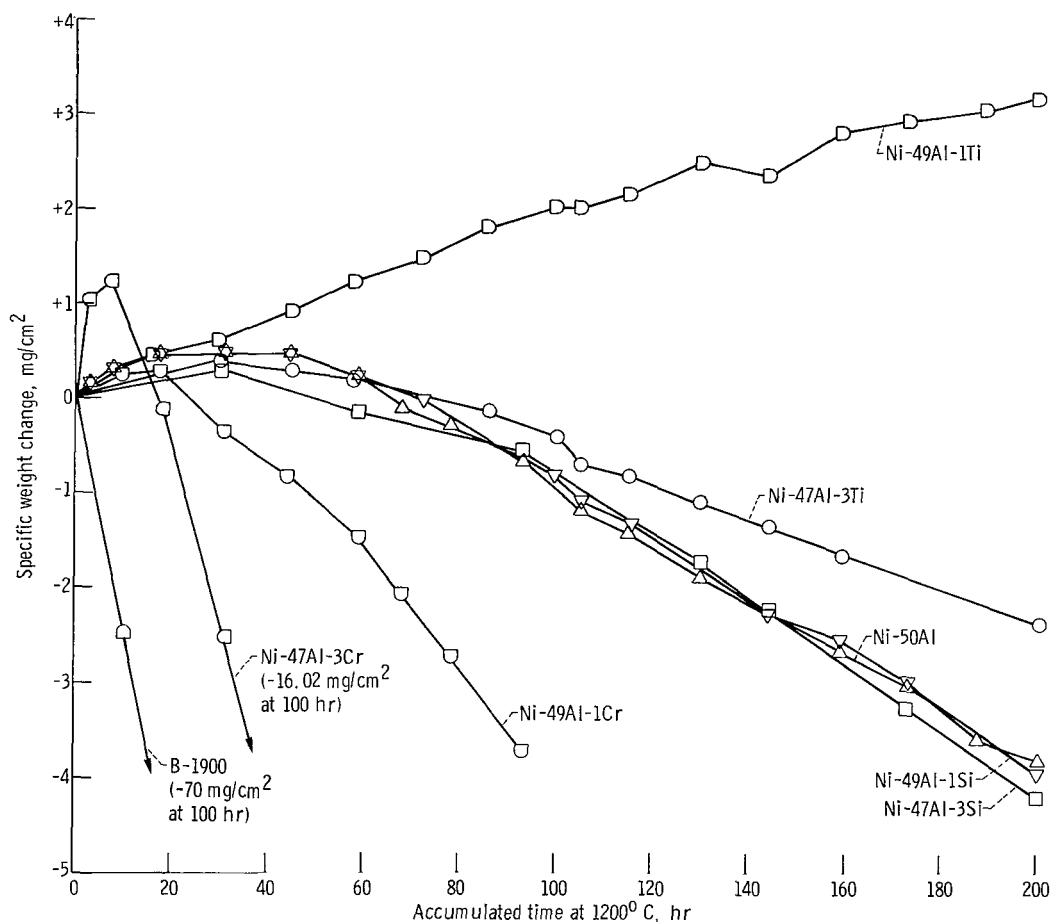


Figure 4. - Cyclic oxidation data for  $\beta$  alloys compared with data for the B-1900 alloy. Compositions of alloys given in atomic percent.

percent-Cr alloy, which lost about the same amount as unalloyed  $\gamma'$ . Since the weight changes of  $\beta$  compositions were slight, those alloys with the least weight losses were oxidized for longer times (200 cycles instead of 100). The Si additions did not significantly affect the weight change of the  $\beta$  alloys. This is in contrast to their effect on the  $\gamma'$  alloys. The Ti additions, however, substantially decreased the weight loss of  $\beta$ . In fact, the  $\beta$  - 1-atomic-percent-Ti alloy gained weight for the entire 200 cycles, the only alloy in the entire study which did. As in the case of the  $\gamma'$  alloys, Cr additions to  $\beta$  increased the amount of weight loss.

Although weight change has become the classic measurement by which comparative oxidation resistance is judged, it is not an unambiguous criterion. Weight change values can be misleading because of vaporization of alloy or scale components and/or spalling of scales. Since the actual amount of metal consumed (or appreciably altered) is a more realistic measure of oxidation resistance, a determination of sample-thickness change

might be a more meaningful measurement than weight change. Thus, in this study we report both weight change as a function of time and final thickness change.

## Metal Recession

Thickness-change data are given in figure 5 for  $\gamma'$  alloys and in figure 6 for  $\beta$  alloys. For the  $\gamma'$  alloys, two values are recorded - the metal loss per side and the thickness of a depletion zone. This depletion zone is thought to be a surface layer of  $\gamma$  and is discussed more fully in the section dealing with metallography and electron microprobe analysis.

As shown in figure 5, the total alloy recession (metal loss and depletion-zone thickness) of  $\gamma'$  is increased by Cr additions, essentially unaffected by Ti, and significantly decreased by Si. The improvement brought about by the addition of 1 atomic percent Si is indeed outstanding, as the oxidation resistance is comparable to that of the unaltered  $\beta$  composition, which is generally considered to have good oxidation resistance (see fig. 6). The B-1900 alloy exhibited more total alloy recession than any of the experimental  $\gamma'$  compositions.

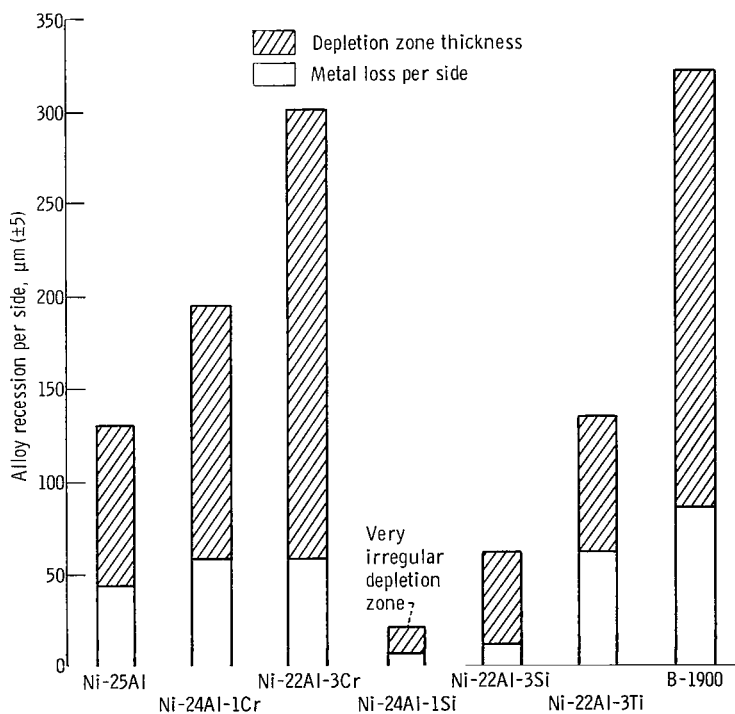


Figure 5. - Recession data for  $\gamma'$  alloys compared with data for the B-1900 alloy after 100 one-hour cycles at  $1200^{\circ}\text{C}$ . Alloy compositions given in atomic percent.

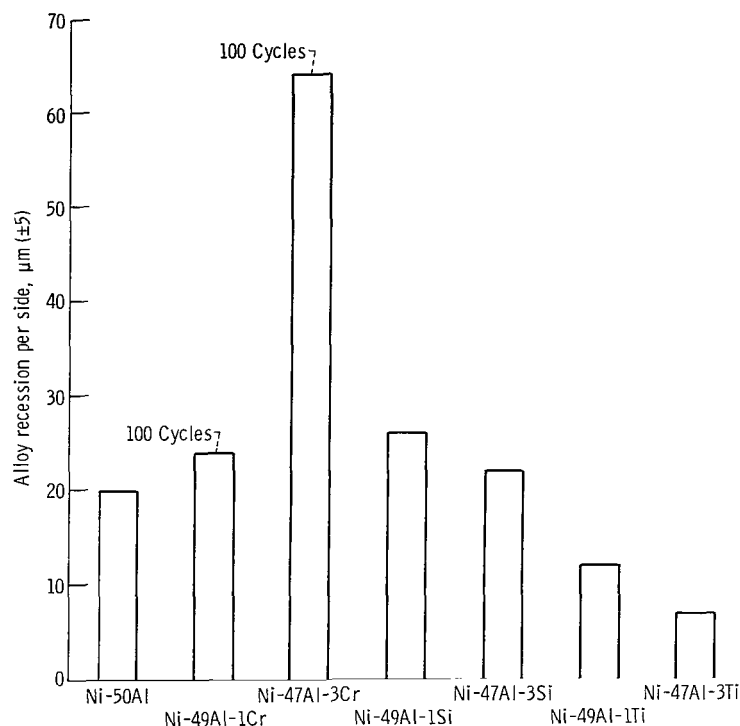


Figure 6. - Recession data for  $\beta$  alloys after 200 one-hour cycles (except where noted otherwise) at  $1200^{\circ}\text{C}$ . Alloy compositions given in atomic percent.

Figure 6 depicts the metal recession experienced by the  $\beta$  compositions. No depletion zones were noted in any of these alloys. In figure 6, an extremely detrimental effect of Cr is noted. Within the limits of the thickness measurements ( $\pm 5 \mu\text{m}$ ), the Si additions appear to have no significant effect on the recession of  $\beta$ , and any beneficial effect of Ti must be considered small.

A comparison of the weight and thickness data for  $\beta$  and  $\beta + 1$  percent Ti indicates that the Ti addition has resulted in some improvement in spall resistance of the  $\text{Al}_2\text{O}_3$  scale. However, any improvement is clouded by the error in the thickness measurements.

## X-Ray Diffraction

Except for the alloy with the Ti addition, all of the  $\gamma'$  alloys had the same oxide phases both retained on the samples and in their spalls (see table II(a)). These oxides were NiO,  $\text{NiAl}_2\text{O}_4$ , and  $\text{Al}_2\text{O}_3$ . The  $\gamma' - 3$ -atomic-percent-Ti sample had, in addition to these oxides,  $\text{NiTiO}_3$  in the spall. The oxides formed on B-1900 were NiO,  $\text{Al}_2\text{O}_3$ ,  $\text{NiAl}_2\text{O}_4$ , and a trirutile structure of undetermined composition. In the B-1900 spalls,

TABLE II. - X-RAY DIFFRACTION DATA FOR  $\gamma'$  AND  $\beta$   
ALLOYS AND FOR THE B-1900 ALLOY AFTER  
100 ONE-HOUR CYCLES AT 1200° C

(a)  $\gamma'$  alloys and B-1900 alloy

Alloy (a)	Retained scale		Spall	
	Oxide	Pattern intensity	Oxide	Pattern intensity
Ni-25Al	NiO	Strong	NiO	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Medium	NiAl <sub>2</sub> O <sub>4</sub>	Medium
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Medium	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Medium
Ni-24Al-1Cr	NiO	Strong	NiO	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Medium	NiAl <sub>2</sub> O <sub>4</sub>	Weak
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak
Ni-22Al-3Cr	NiO	Strong	NiO	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Weak	NiAl <sub>2</sub> O <sub>4</sub>	Medium
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak
Ni-24Al-1Si	NiO	Strong	NiO	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Weak	NiAl <sub>2</sub> O <sub>4</sub>	Weak
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak
Ni-22Al-3Si	NiO	Strong	NiO	Strong
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Strong	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Weak	NiAl <sub>2</sub> O <sub>4</sub>	Weak
Ni-22Al-3Ti	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Strong	NiO	Strong
	NiAl <sub>2</sub> O <sub>4</sub>	Medium	NiAl <sub>2</sub> O <sub>4</sub>	Medium
	TiO <sub>2</sub>	Weak	NiTiO <sub>3</sub>	Weak
B-1900	NiO	Strong	NiO	Strong
	Trirutile	Strong	Trirutile	Medium
	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	Weak	Spinel	Weak
	Spinel	Weak		

(b)  $\beta$  alloys

Alloy (a)	Retained scale	Spall
Ni-50Al	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	$\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-49Al-1Si	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	$\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-47Al-3Si	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	$\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-49Al-1Ti	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	<sup>b</sup> $\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-47Al-3Ti	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	<sup>b</sup> $\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-49Al-1Cr	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	$\alpha$ Al <sub>2</sub> O <sub>3</sub>
Ni-47Al-3Cr	$\alpha$ Al <sub>2</sub> O <sub>3</sub>	$\alpha$ Al <sub>2</sub> O <sub>3</sub>

<sup>a</sup>Alloy compositions in atomic percent.

<sup>b</sup>Assumed oxide; insufficient sample for analysis.

$\text{Al}_2\text{O}_3$  was not found, but  $\text{NiO}$ ,  $\text{NiAl}_2\text{O}_4$ , and the trirutile oxide were.

Only  $\text{Al}_2\text{O}_3$  was found on the  $\beta$  alloys (see table II(b)). The spalls from these alloys were sparse and, therefore, meaningful X-ray diffraction results were most difficult to obtain. However, since only  $\text{Al}_2\text{O}_3$  was found on all  $\beta$  alloys in situ, it seems reasonable to assume that the small amount of spall must have consisted of  $\text{Al}_2\text{O}_3$  also. For those oxides which exist over a range of compositions (i.e.,  $\text{NiO}$  and the spinels), differences in lattice parameters were sought. However, no meaningful differences among the oxides of the same class were found.

## Metallography and Electron Microprobe Analysis

All of the  $\gamma'$  alloys had similar microstructures. Typical of these microstructures is that of the  $\gamma'$  - 3-atomic-percent-Si alloy (fig. 7) after 100 cycles at  $1200^\circ\text{C}$ . It is distinguished by a large grain size and a surface depletion zone. A sharp boundary separates the depletion zone from the interior of the sample. Such surface layers were previously found on these alloys after  $1100^\circ\text{C}$  exposure (ref. 12) and identified as nickel solid solution ( $\gamma$ ).

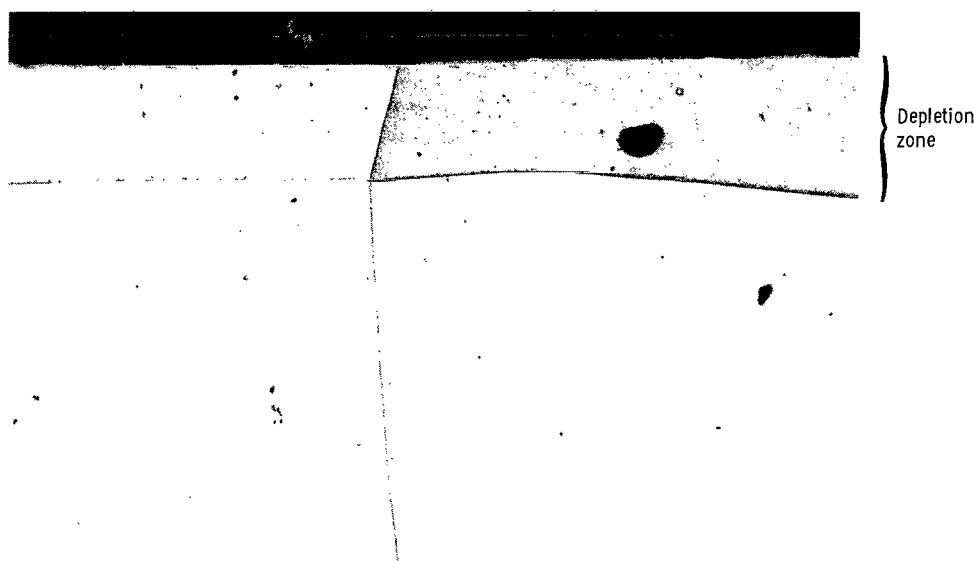


Figure 7. - Microstructure of nickel - 22-atomic-percent-aluminum - 3-atomic-percent-silicon alloy ( $\gamma'$ ) after 100 one-hour cycles at  $1200^\circ\text{C}$ . (Note depletion zone, with sharp boundary.) This structure is typical of all  $\gamma'$  alloys tested. Sample etched; X250.

To confirm the earlier evaluation of the depletion zone (ref. 12), an electron microprobe analysis was performed on the  $\gamma'$  - 3-atomic-percent-Si sample. Figure 8 illustrates the results of that analysis. The sharp boundary of the microstructure is associated with a sharp drop in Al and Si. To determine if this depletion was accompanied by a phase change, the oxide and mounting material were stripped from the alloy. Powder samples were then ground from the surface, and X-ray diffraction analysis was performed on these samples. This analysis showed that the surface layer had transformed to  $\gamma$ .

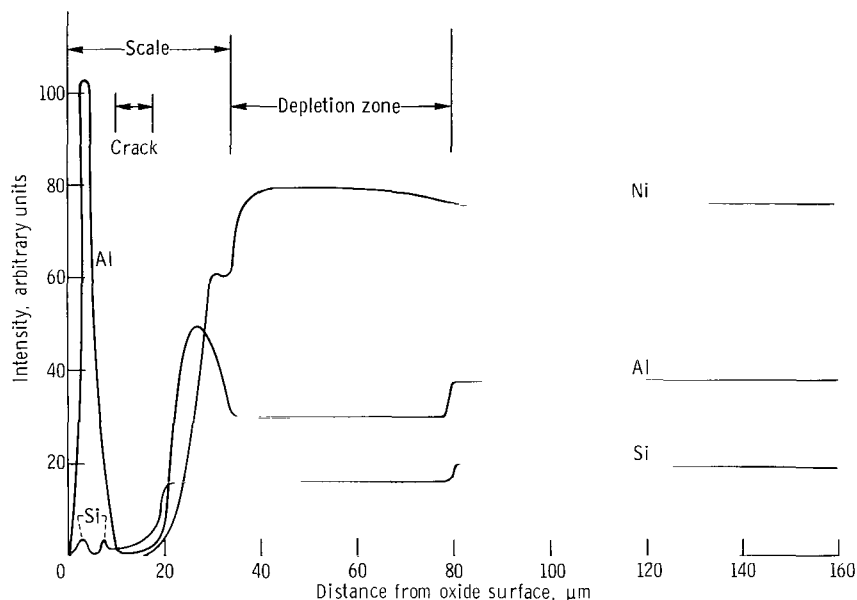


Figure 8. - Microprobe traces of nickel - 22-atomic-percent-aluminum - 3-atomic-percent-silicon alloy ( $\gamma'$ ) after 100 one-hour cycles at 1200°C.

One might expect that once a layer of  $\gamma$  was formed at the oxide-metal interface, the oxidation rate would accelerate to that of  $\gamma$ . However, this does not occur. Therefore, the oxidation behavior must not be controlled by the depletion-zone composition. Instead, the oxide, which never completely spalls and whose initial composition was determined by the original  $\gamma'$ , probably influences the oxidation in its latter stages.

Another feature of interest in figure 8 is the indication of some Si in an otherwise Al-rich scale. Although the form or distribution of this Si in the scale is presently not known, its presence in the scale is probably responsible for the noted improvement in oxidation resistance of the Si-containing  $\gamma'$  compositions.

The microstructure of B-1900 is shown in figure 9. The interior of the sample is  $\gamma$

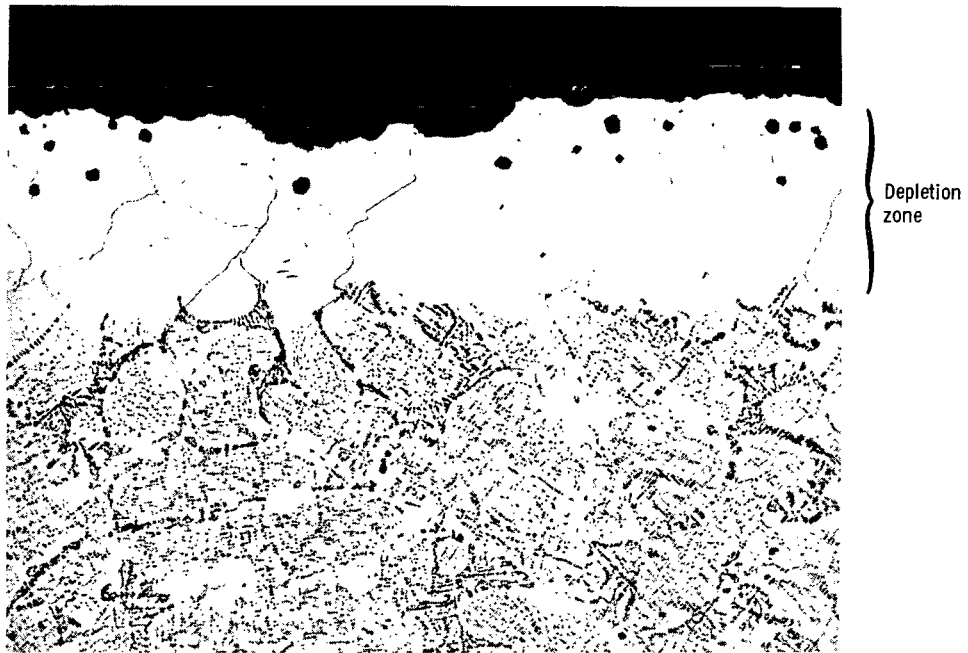


Figure 9. - Microstructure of B-1900 alloy after 100 one-hour cycles at 1200° C. (Note surface depletion.) Sample etched; X100.



Figure 10. - Microstructure of nickel - 49-atomic-percent-aluminum - 1-atomic-percent-titanium alloy (B) after 200 one-hour cycles at 1200° C. (Note uniform oxidation, with no depletion zone.) Sample etched; X500.

and  $\gamma'$ , with carbides primarily at the grain boundaries. On the outside edges is a depletion zone of  $\gamma$ . This zone also contains what appear to be pores near the surface, which may be Kirkendall voids.

The  $\beta$  alloys all have similar microstructures. They are typified by the  $\beta + 1$ -atomic-percent-Ti alloy shown in figure 10. This microstructure consists of large grains with no evidence of a depletion zone.

## SUMMARY OF RESULTS

In this investigation, samples of nickel-aluminum alloys  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ) and  $\text{NiAl}$  ( $\beta$ ) with and without small additions (up to 3 at. %) of chromium, silicon, and titanium were oxidized. The commercial nickel-base superalloy B-1900, which is typical of  $\gamma'$ -strengthened nickel-base alloys, was oxidized for comparison. Alloy B-1900 is one of the more oxidation-resistant alloys. The samples were exposed to static air at  $1200^\circ\text{C}$  for up to 200 cycles. Each cycle consisted of 1 hour at temperature followed by 40 minutes of air cooling. The degree of attack was judged primarily by metal recession, supplemented by specific weight changes, metallography, electron-microprobe analysis, and X-ray diffraction. The results of this investigation may be summarized as follows:

1. As a class, the  $\gamma'$  compositions oxidized more rapidly than the  $\beta$  compositions.
2. Silicon additions to  $\gamma'$  compositions decreased the metal loss to values about the same as those for the pure  $\beta$  compositions. However, this decreased metal loss of  $\gamma'$  compositions is accompanied by the formation of a surface depletion zone. The formation and the effect of this zone on oxidation resistance are not fully understood.
3. Titanium had little effect on the oxidation resistance of  $\gamma'$  compositions.
4. Chromium additions to the  $\gamma'$  composition decreased its oxidation resistance substantially, with the addition of 3 atomic percent chromium being more deleterious than the addition of 1 atomic percent.
5. The B-1900 alloy oxidized the same as the Ni-22Al-3Cr alloy.
6. Titanium additions offered only a slight improvement to the oxidation resistance of the  $\beta$  composition.
7. Silicon additions had little effect on the oxidation of the  $\beta$  composition.
8. Chromium additions, especially 3 atomic percent chromium, markedly decreased the oxidation resistance of the  $\beta$  composition.

## CONCLUDING REMARKS

Small third element additions can substantially alter the cyclic oxidation resistance

of the nickel-aluminum alloys  $\text{Ni}_3\text{Al}$  ( $\gamma'$ ) and  $\text{NiAl}$  ( $\beta$ ). However, this determination requires sufficiently severe test conditions (for the present investigation,  $1200^\circ\text{C}$  for up to 200 one-hour cycles). This is especially true in the case of the  $\beta$  alloys, for which lower temperature tests could not differentiate the effects of chromium, silicon, and titanium.

If the silicon improvements on  $\gamma'$  could be translated to superalloys, their oxidation would be nearly that of current  $\text{NiAl}$ -coated alloys. This possibility may be particularly applicable for alloys containing a high volume percent of  $\gamma'$ , such as NX-188 of Pratt & Whitney Aircraft, NASA WAZ-20, and B-1900. Presently, B-1900, NX-188, and WAZ-20 contain silicon only as a tramp element impurity. The effect of silicon additions on the oxidation behavior of such complex alloys is not easy to predict on the basis of the behavior of ternary alloys. But, it would be interesting to observe the effects of 1- to 3-atomic-percent additions of silicon to these superalloys of high  $\gamma'$  content. A more systematic approach which might lend itself to easier interpretation would be the inclusion of silicon additions to experimental two-phase ( $\gamma + \gamma'$ ) binary nickel-aluminum compositions. Specifically, attempts should be made to find the optimum compositions and to discover the causes of improvement. A knowledge of the causes might lead to a discovery of other additions which could lead to even greater improvement to the oxidation resistance of this system.

Additions of titanium to  $\beta$  alloys improve spall resistance; however, this improvement is not reflected as any substantial lowering of metal recession. This suggests that the addition of titanium to aluminide coatings is not likely to be markedly advantageous.

While silicon additions have no apparent effect on the oxidation of  $\beta$ , they may be of long-time benefit in a coating application. This benefit might occur in the final stages of coating life, when the  $\beta$  has lost sufficient aluminum to transform into  $\gamma'$ . At this point, the silicon might appreciably extend the lifetime of the coating.

Also of interest to coating work is the deleterious effect of chromium on the oxidation of  $\beta$ . This is especially interesting inasmuch as chromium is often added in commercial coatings to improve hot corrosion resistance. It appears that the benefits in hot corrosion will have to be carefully weighed against the losses in oxidation resistance.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, April 4, 1972,  
134-03.

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